# Electronic Structure of $Ti_xC_{60}$ Fullerides Studied by X-ray Emission Spectroscopy

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## ABSTRACT

For metal-fullerene compounds, it has been found that metal atoms can be bonded to fullerenes, resulting in different structures.[1] Some of the alkali and alkaline-earth metal intercalated $C_{60}$ compounds have shown the properties of superconductivity.[2] According to the estimation of the energetical calculations, based on the assumption of the ionic bonding, the stable metal-$C_{60}$ compounds are only those with alkali and alkaline-earth metals, or mercury.[3] However, several studies have shown some evidences that transition-metal fulleride can be formed.[4-6] The results suggest that the bond in this compound is covalent-like with a partial charge transfer from Ti to $C_{60}$. No detailed information of the exact bond nature was obtained in those studies and the further studies with complementary techniques are required.

In this work we present the results from C $K\alpha$ x-ray emission of $Ti_xC_{60}$. Our results demonstrate that the combined measurements of absorption and emission spectra can be used to provide electronic structure information of molecules. The information is element specific and selective and so is useful for the study of hybridization and bonding. This method has been successfully employed for the electronic structure analysis of fullerenes.[7, 8]

The samples were made by co-evaporation of $C_{60}$ and titanium from a Knudsen-type effusion cell and an e-beam evaporator, respectively. Films deposited in an ultrahigh vacuum growth chamber. After co-evaporation, a vanadium capping layer (~ 500Å) was deposited on the surface of the sample to protect it from oxidation during the delivery for XES measurement. The preparation and characterisation of the films have been described in detailed in Ref. 6.

XES experiments were performed at beamline 7.0. A grazing incident soft x-ray fluorescence spectrometer (Grace) was used to measure the x-ray emission spectra.[9] Figure 1 displays non-resonant (**a**) and resonant (**b**) XES spectra of $Ti_xC_{60}$, and $C_{60}$ films with the excitation energy of 300 eV and 284.5 eV, respectively. The spectrum from the $Ti_{2.1}C_{60}$ sample exhibits a similar profile with respect to the energy position and intensity distribution of the pure $C_{60}$ emission bands. The one for $Ti_{3.6}C_{60}$ presents the same linewidth as to pure $C_{60}$ with respect to the total emission band, but the sub-band structures are smeared out. The emission band $E_3$ for $Ti_{3.6}C_{60}$ has a small shift towards to lower photon energy, showed in Fig.1 (**a**).

With 284.5 eV photon excitation, resonant XES spectra of $Ti_xC_{60}$ and pure $C_{60}$ were obtained and shown in Fig. 1 (**b**). A sharper peak of the emission at 284.5 eV, marked as $e$, appears due to the processes of atomic recombination and diffuse scattering. Five distinguishable emission bands are resolved in the resonant XES spectrum of $C_{60}$. According to *ab initio* Hartree-Fock frozen orbital model calculations,[10] the first emission band $E_1$ corresponds to the highest occupied molecular orbital of $C_{60}$ with the $4h_u$ symmetry, while the second band $E_2$ represents a combination of the nearly degenerate $4g_g$ and $7h_g$ orbitals of $C_{60}$. Bands $E_3$ and $E_4$ contain more

complicated molecular orbital combinations, in which are included three $h_g$, three $g_u$, one $h_u$, one $g_g$, one $a_g$, and one $t_{1u}$ states. Band $E_5$ contains the $2h_u$, $3t_{1u}$ and $2g_g$ orbitals of $C_{60}$. The resonant XES spectrum of $Ti_{2.1}C_{60}$ shows similar spectral profiles of these emission bands to the one of the pure $C_{60}$. Some intensity variations, compared with pure $C_{60}$, were observed for the bands $E_1$, $E_2$, and $E_5$. The observed variations of the intensities for these emission bands upon the excitation energy in the case of pure $C_{60}$, has been assigned as a result of symmetry selectivity and parity conservation of the resonant inelastic x-ray scattering process.[10, 11] The spectrum from $Ti_{2.1}C_{60}$ sample shows a decrease in intensity of the emission bands $E_1$ and $E_5$, which may indicate that the formation of a new compound phase reduces the symmetry. With the increase of titanium content, the structures for these bands are smeared out and the intensity of $E_5$ band was further decreased in the resonant spectrum of $Ti_{3.6}C_{60}$.
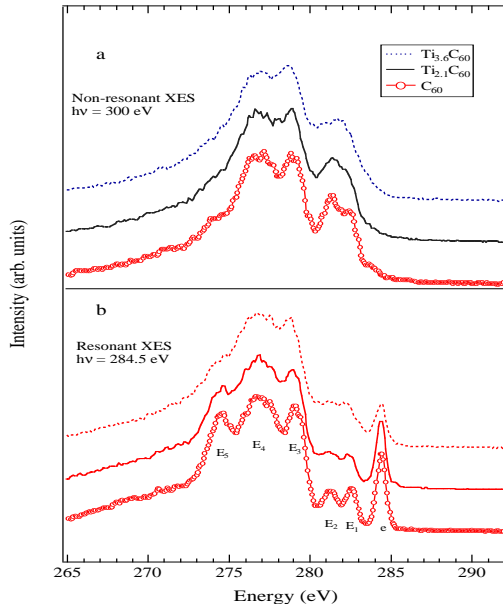


Figure 1 (**a**) C $K\alpha$ non-resonant XES spectra of $Ti_xC_{60}$ and $C_{60}$ films, excited by the photons with the energy of 300 eV. (**b**) C $K\alpha$ resonant XES spectra of $Ti_xC_{60}$ and $C_{60}$ films, excited by the photons with the energy of 284.5 eV.
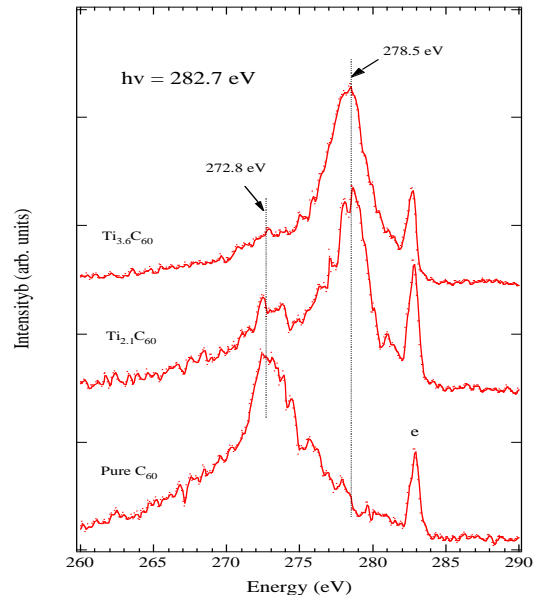


Figure 2. C $K\alpha$ resonant inelastic x-ray scattering spectra of $Ti_xC_{60}$ and $C_{60}$ films with the excitation energy of 282.7 eV. The spectra are smoothed using a binomial method.

Figure 2 shows XES spectra structure of $Ti_xC_{60}$ and $C_{60}$ films with detuning the excitation energy to 282.7 eV (at 1.8 eV below the $C1s$ absorption threshold). For the $Ti_{2.1}C_{60}$ sample, at 272.8 eV, the peak has decreased obviously and is smeared out in $Ti_{3.6}C_{60}$, indicating Ti atom has bonded with carbon atom of $C_{60}$. Whereas the emission intensity of the peak from pure $C_{60}$ has been almost depleted for both samples. Only a weak peak can be observed for $Ti_{2.1}C_{60}$ and $Ti_{3.6}C_{60}$ at the same energy position as the peak of pure $C_{60}$ (272.8 eV). Also the intensity of this $C_{60}$ characteristic peak decreases as the titanium concentration increases. Thus, one can attribute the structures in the spectrum of $Ti_{2.1}C_{60}$ film to the formation of the chemical bonding between Ti and $C_{60}$ cage. These featrues also exsited the spectrum of $Ti_{3.6}C_{60}$ film but it is broaden at 278.5 eV, which reveals the tendency forwards titanium carbide, $i.e.$, $C_{60}$ cage may start to be broken at this concentration of titanium.

The C $K\alpha$ x-ray emission spectra of the $Ti_xC_{60}$ films show the same total emission bandwidth as that from the pure $C_{60}$ sample. Resonant and non-resonant XES spectra of the $Ti_{2.1}C_{60}$ film exhibit an x-ray spectral shape similar to pure $C_{60}$, while the spectra of $Ti_{3.6}C_{60}$ film show some amount of contribution from the titanium carbide phase**.** All the experimental results indicate that a titanium fulleride is formed in the co-evaporation process of $C_{60}$ and titanium, although some evidences for titanium carbide formation was obviously observed for $Ti_{3.6}C_{60}$ film.

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